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Influence of hypoxia on silicate concentrations in the Baltic Proper (Baltic Sea)

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Silica (Si) is a key nutrient for diatoms. Over the last century, Si concentrations within the Baltic Sea decreased significantly. This is mainly attributed to ongoing eutrophication, increased production and subsequent deposition and accumulation of organic matter including biogenic silica. As a consequence of the eutrophication, hypoxic and anoxic bottom waters have spread affecting nutrient cycling. This paper looks at the potential impact of oxygen on dissolved silica (DSi). It presents a statistical analysis of the relationship between DSi concentrations and oxygen conditions (O_2) in the deep water of the Baltic Proper. The idea is not new, but this is the first time it is studied in more detail in this area. Regression analysis shows that DSi concentrations decrease significantly with O_2 concentrations, and that the major intrusion of saline water in 1993 strengthened this relationship. Increased hypoxia will significantly affect the cycling of Si in the Baltic Sea.

Introduction

The Baltic Sea is a brackish and semi-enclosed water body with limited water exchange with the North Sea through the Danish Straits. This has resulted in long water residence times of more than 30 years (Papush *et al*. 2009). Major Baltic inflows (MBI) of saline water provide a supply of oxygen to the deep waters of the Baltic (Matthäus 2006). They also strengthen the salinity stratification which decreases the oxygen exchange between the deep water and the surface waters. During periods of weak stratification, in-between the large inflows, large areas can benefit from improved oxygen conditions as the volume of surface layers increase (Stigebrandt and Gustafsson 2007). These MBIs are infrequent and irregular, and stagnation periods in the deeper water can last a decade or more (Reissman *et al*. 2009).

Hypoxia has been intermittently present since the formation of the Littorina Sea (ca. 8000 cal. yr BP) as a result of a natural climate-driven phenomenon. However, the spatial extent as well as the intensity of hypoxia have increased significantly with eutrophication (Zillén *et al*. 2008). In the 1950s–1960s, the extent of bottom areas with laminated sediments increased markedly in the Baltic Proper as a response to large inputs of organic material (Zillén *et al*. 2008). At the same time there were indications of an increased production and shifts in diatom assemblages (e.g. Ellegaard *et al*. 2006, Weckström *et al*. 2007). Today, the Baltic Sea has some of the highest percentages of seasonally hypoxic and permanently anoxic areas of all the world's marine

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areas (Diaz and Rosenberg 2008). On average, the area covered by hypoxic water is ~50 000 km^2 (1961–2005), although the inter-annual variation is significant due to the variation in stratification (Savchuk 2010).

In addition to the variation in the inflow of oxygenated water, eutrophication has also had a major impact on the distribution of hypoxia (Gustafsson 2012). In general, coastal eutrophication has caused extensive hypoxia in seas around the world (Diaz 2000), largely attributable to the increased production and sedimentation of organic material that occurs during eutrophication. Significant quantities of oxygen are consumed during the degradation of this material, causing decreases in the deep water's oxygen content and in some cases also lead to a production of hydrogen sulphide. Based on paleoecological studies of the Baltic Sea sediments, signs of eutrophication, such as changes in the diatom assemblage composition, occurred already 100–150 years ago (Andrén 1999, Weckström 2006). Other evidence of human-induced eutrophication caused by increased nutrient load were identified in the water mass in the beginning of the 1950s (Elmgren 2001). Major increases in the nitrogen (N) and phosphorus (P) loads to the Baltic Sea occurred in the 1970s–1980s (Stålnacke *et al.* 1999), leading to significant increases in N and P concentrations in the water mass between the 1970s and the 1990s. The concentrations of these elements in the Baltic Sea have since declined slightly (Papush and Danielsson 2006).

DSi is essential for diatoms that dominate spring blooms (up to 80%–90% of the total spring bloom; Jurgensone *et al.* 2011). The availability of DSi can limit the spring bloom and lead to a shift from diatoms to dinoflagellates (Tallberg *et al.* 2012). A recent model of the silica budget in the Baltic Sea suggests that deep hypoxic/anoxic areas may act as internal sources of DSi (Papush *et al.* 2009). DSi in the Baltic Sea originates from weathering of bedrock and soil. In a long term, the DSi load to the Baltic Sea has decreased over time due to damming of its catchment. Within the Baltic Sea, DSi concentrations have decreased significantly (Papush and Danielsson 2006) due to eutrophication as a consequence of increased primary production and sedimentation. The changes in DSi concentrations are more dramatic than those seen for nitrogen and phosphorus, and the levels have become so low that quality and quantity of the sea's primary production are under threat (Danielsson *et al.* 2008, Olli *et al.* 2008).

Despite evidences that redox can affect nutrient dynamics, there are relatively few studies of oxygen conditions and DSi. The aim of this study was to statistically analyse the relationship between DSi and oxygen concentrations in the deep waters of the Baltic Proper. The analyses were based on data acquired during national monitoring programs conducted between 1970 and 2010. Data from 16 deep stations in waters with varied conditions, including both oxic and hypoxic/anoxic environments, were examined.

Study area

The non-tidal Baltic Sea is located in northern Europe (Fig. 1). It is the world's largest body of brackish water (373 000 km^2, 21 000 km^3) with a drainage area fourfold larger than the sea surface area, and a human population of ca. 84 million living in its vicinity (Hannerz and Destouni 2006). The Baltic Sea can be divided into a number of sub-basins separated by sills. The present study focused on the largest sub-basin — the Baltic Proper — which shows a number of signs of eutrophication, including low oxygen concentrations or anoxia in the bottom waters.

Hydrography

The entrance sills between the Kattegat and the North Sea act as barriers that restrict water exchange and give the Baltic a long water residence time of 15–35 years (Matthäus and Schinke 1999, Papush *et al.* 2009). Major inflows from the North Sea are controlled by atmospheric forcing (Stigebrandt 2001). They mainly occur during winter when stronger than average westerly winds last over periods of days to weeks (Danielsson *et al.* 2007). These major saltwater inflows are unpredictable and infrequent. Over the last few decades, they occurred four times only: in 1974, 1993, 1997 and 2003

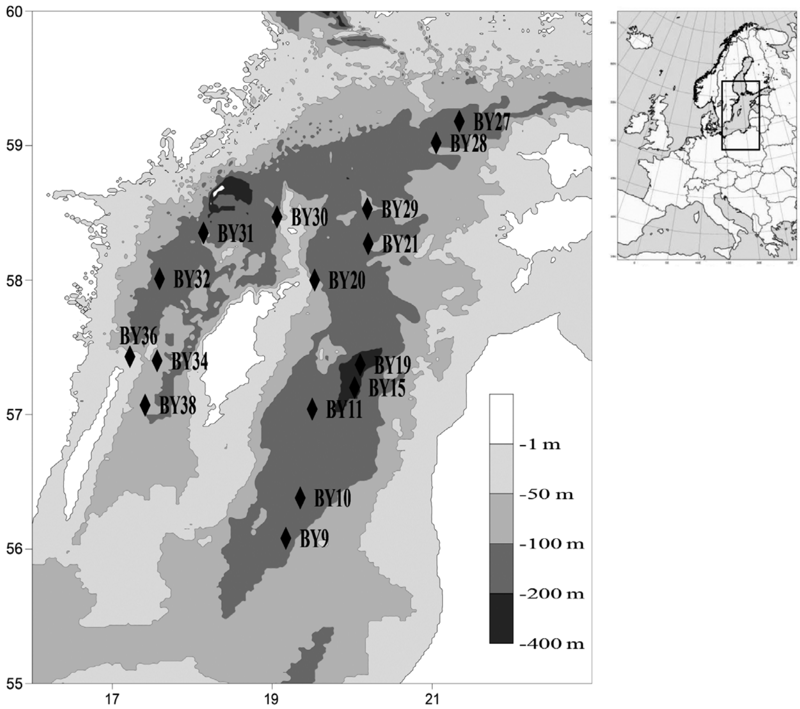

Fig. 1. The bathymetry of the study area. The locations of the monitoring stations are also shown.

(Matthäus 2006). In addition to these larger events there were several less significant ones that ventilate the intermediate layers just below the halocline (Stigebrandt 2001, Elken and Matthäus 2008). During the periods of stagnation in-between, there is a freshening of the surface waters and a continuous downward movement of the halocline and oxycline (Conley *et al*. 2002).

In addition to transporting O_2 to the bottom waters, intrusions of saline water also affect the strength of the halocline. From 1959 to 1993, the strength of the Baltic halocline generally decreased (Rahm and Danielsson 2001). The 1980s and 1990s were characterised by high precipitation, which led to an increased runoff volume and thus a decrease in salinity. This was partly responsible for the occurrence of a long period of "stagnation" of the deep waters. The major inflow in 1993 contributed to the restoration of the halocline's strength. However, in conjunction with the windy winters of the early 1990s, the inflow also reduced the halocline's stability, increasing the diffusive fluxes across it (Stigebrandt and Gustafsson 2007).

Reducing conditions in the bottom waters are a consequence of low ventilation and high remineralisation of organic matter. Anoxic conditions occur if the rate at which oxygen is consumed exceeds the rate at which it is imported from overlying waters and/or neighbouring areas. The deeper parts of the Baltic Sea have stagnant water masses below the halocline that can easily become anoxic; this occurred in the (geological) past (Zillén *et al*. 2008). In 2010, the Swedish Meteorological and Hydrological Institute (SMHI) carried out an extensive survey of bottom conditions in the Baltic Proper (Hansson *et al*. 2010). They found that ~28% of the bottom area was anoxic, and that almost 20% of the bottom water contained hydrogen sulphide. This is the largest anoxic bottom area observed since the start of more regular monitoring in the 1960s.

Silica cycling

Long-term decreases in DSi concentrations have been observed in aquatic ecosystems around the world (Billen and Garnier 2007, Conley *et al*. 2008). The nutrient loads of these systems are all affected by human activities, e.g. eutrophication. The decreases in DSi concentrations are attributed to the formation of intense diatom blooms, which are followed by sedimentation of biogenic silica exhausting the DSi pool in the water column (Schelske *et al*. 1983). In the Baltic Sea, the rate of Si accumulation in sediments increased by a factor of 1.9 during the 20th century due to increased diatom production (Conley *et al*. 2008).

Silica is a product of weathering. The major DSi load comes from the northern parts of the Baltic Sea (Papush and Danielsson 2006, Humborg *et al*. 2008). These loads declined by 30%–40% over the 20th century due to increased retention within the sea's catchments (Humborg *et al*. 2008). Within the Baltic, DSi is transported towards the south, from the Gulf of Bothnia to the Kattegat, primarily along the western coast of the Baltic (Rahm and Danielsson 2007). In total, ~70% of the DSi river load is retained within the Baltic, primarily in the eastern regions (Papush *et al*. 2009). The DSi concentrations in the photic zone exhibit a characteristic pattern that is related to seasonal changes in the weather, Si loads, and primary production; the highest concentrations occur in winter and the lowest in summer (Papush and Danielsson 2006). From a historical perspective, silica concentrations have decreased from their "pristine" level of roughly 36 μM to their current value of about 13 μM (Conley *et al*. 2008). Most of this decline occurred some decades ago. Over a much shorter timescale (1970–2000), Si concentrations underwent annual decreases of 0.05 to 1.2 μmol Si l^{-1} yr^{-1} (Papush and Danielsson 2006). Because of this decrease, the concentration of DSi and the Redfield ratio indicate that during the diatom spring bloom DSi concentrations can decrease drastically and the spring bloom may become Si-limited in some regions (Danielsson *et al*. 2008).

Spreading of hypoxic/anoxic areas and decreasing oxygen concentrations within the sediments increase the flux of inorganic nutrients, including DSi into the overlaying water mass (Rabalais *et al*. 2010). This has also been found in the Baltic Sea (Papush *et al*. 2009, Tallberg *et al*. 2012). The sediments become an internal source and affect the nutrient recycling processes that fuel eutrophication. The release of phosphorus (P) from Fe oxides in the surficial sediments of the bottom waters is promoted under hypoxic/anoxic conditions (Mort *et al*. 2010). This results in internal cycling of P that is likely to fuel primary production and thus contributes to the maintenance of low oxygen conditions (van Capellen and Ingall 1994). It has also been suggested that denitrification, which is intensified by deep water stagnation, might exert long-term control over the winter concentration of inorganic nitrogen compounds (Kuparinen and Tuominen 2001).

Data and statistical analyses

The data set was retrieved from the Swedish Ocean Archive (SHARK) database, which is maintained by the Swedish Meteorological and Hydrological Institute (SMHI). The data originate from the Swedish National Environmental Monitoring Programme coordinated by the Swedish EPA. Observations from the years between 1970 and 2010 were examined. Dissolved silica concentrations were determined using the procedures recommended by HELCOM (2000), which are based on the molybdate method using ascorbic acid as the reductant developed by Grasshoff *et al*. (1983). The hydrography variables include measurements of the oxygen and hydrogen sulphide concentration, temperature, and salinity. For convenience, anoxia is reported as "negative" oxygen computed from the amount of oxygen equivalent to oxidize the hydrogen sulphide present in the bottom waters (Fonselius 1981).

Sixteen stations (*see* Fig. 1) with water depths of at least 100 m were chosen to ensure that the studied data accurately reflected the conditions below the halocline. In addition, all stations were in areas, where bottom water had been hypoxic or anoxic at some point (Table 1). All stations are sampled more often than once a year. From the 1990s and onwards the regular monitoring stations (BY10, BY15, BY20, BY29, BY31, BY32 and BY38) include > 50 sampling events per year. For three stations (BY11, BY19 and BY21), data were only available from 1992 onwards, and for station BY34 data was available only up to 1992.

The average deep water DSi concentrations varied between 45.5 μmol l^{-1} (station BY21) and 72.5 μmol l^{-1} (station BY15). The measured salinity concentrations were dependent on the stations' distance from the saline North Sea, the water depth and the general anti-clockwise circulation of water in the Baltic Proper. Low O_2 concentrations were recorded at most of the stations examined for almost the entire period studied. The only station at which oxic conditions were found during a substantial number of events, ~40%, was BY9 (Table 1 and Fig. 1). More than two thirds of the measurements acquired at the southernmost stations were indicative of anoxic conditions.

From these data, two subsets were created. The first consisted of DSi and O_2 concentrations averaged for each sampling event and represent the means of multiple observations acquired at different water depths below 100 m at each station. This data set is called mean data. The second set features only data from those measurements conducted at maximum depth (i.e. max 1 m above the sea floor) for each sampling event. Since anoxia is most common in the bottom layer, this set should contain a greater proportion of anoxic measurements than the first. This data set is named max data.

Statistical analysis

ANOVA followed by Tukey's multiple comparison test were used to determine whether there were statistically significant differences in DSi means among stations. Pearson's correlation was used to test the correlation between DSi and salinity, temperature respective O2. It was also tested for correlation between DSi and pH.

Stepwise regression analysis was used to determine if and how the variation in DSi concentrations was affected by variation in the measured O_2 concentrations. It is of interest to determine whether the significant influx of saline water in 1993 had any effect on the nature of this relationship. The most common way would probably be to divide the data into two regression models — one before and one after the influx. However, this would not enable statistical testing of whether there was a significant difference in the relationship before and after the influx, but only the dependence for the respective time period. To statistically test the difference in between the periods, a dummy variable was introduced into the regression model. This dummy variable, $D_{70–92}$, takes the value 1 for the years 1970–1992, and 0 for the period 1993–2010. This led to the following regression model:

Table 1. Characteristics of the stations over the time period 1970–2010. WD represents water depth. Salinity and SiO_4 are represented by their overall mean values and Hyp./Anox. is the proportion, over time, the stations have been hypoxic (0–2 ml l^{-1}) or anoxic (< 0 ml l^{-1}).

Station	Lat. (°N)	Long. (°E)	Year	WD (m)	Salinity (PSU)	DSi (μmol l^{-1})	Hyp./Anox. (%)
BY10	56.38	19.35	1975–2010	176	11.8	55.7	32/61
BY11	57.04	19.50	1992–2010	226	12.0	64.3	31/61
BY15	57.20	20.03	1970–2010	245	12.4	72.5	33/64
BY19	57.37	20.10	1992–2010	162	11.5	59.8	27/72
BY20	58.00	19.53	1970–2010	204	11.7	65.5	25/75
BY21	58.27	20.20	1992–2010	132	10.5	45.4	89/7
BY27	59.18	21.34	1970–2010	195	10.4	60.7	52/45
BY28	59.02	21.05	1973–2010	206	10.6	55.8	61/39
BY29	58.53	20.19	1970–2010	187	10.9	55.6	60/40
BY30	58.47	19.06	1975–2010	197	10.4	49.9	94/6
BY31	58.35	18.14	1970–2010	458	10.4	51.8	69/31
BY32	58.01	17.59	1970–2010	211	10.0	54.4	43/52
BY34	57.40	17.56	1970–1992	109	10.0	59.4	75/21
BY36	57.43	17.22	1970–2010	164	9.9	54.0	76/20
BY38	57.07	17.41	1970–2010	115	9.7	54.8	48/44
BY9	56.08	19.17	1970–2010	135	11.3	47.3	55/4

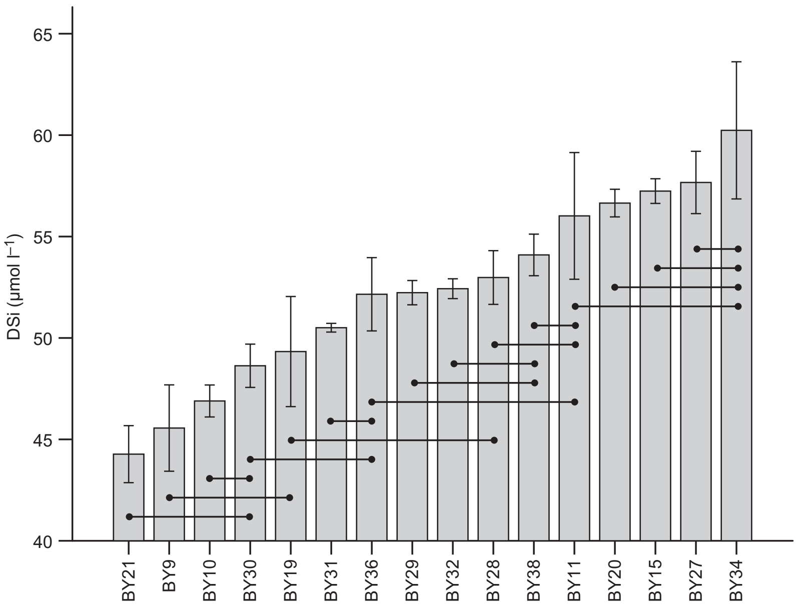

Fig. 2. Bar chart of the median DSi concentrations at different stations. The mean concentrations per station ordered from lowest to highest. The lines join the stations not significantly different from each other. The significances were determined using Tukey's multiple comparison test ($p < 0.05$).

$$DSi = \beta_0 + \beta_1 O_2 + \beta_2 D_{70–92} + \beta_3 D_{70–92} \times O_2 + \varepsilon \quad (1)$$

β_0 is the intercept for 1993–2010 and describes the mean DSi concentrations at the oxygen level of 0 ml l^{-1}, β_1 describes how DSi changes with O_2 during the same period. β_2 is used to test if there is a significant difference in mean DSi concentrations between the two periods. β_3 tests if there is a significantly different relationship between DSi and O_2 concentrations before and after this major salt-water intrusion, i.e. if the slope is significantly different between the two periods.

The regression analyses were performed for all data points and stationwise to see if the relationships differed from station to station. In addition, analyses were performed on both max and mean data sets, i.e. on the data set focusing exclusively on the data set containing the deepest measurements and on that containing data representing averaged concentrations measured at multiple depths.

Results

The mean DSi concentrations differed significantly from station to station (Fig. 2). The mean at BY21 was significantly lower than at all other stations except BY9, BY10 and BY30 (Fig. 2). The mean DSi concentration at BY34 was significantly higher than all other stations except for four stations on the eastern side of the Baltic Proper (BY11, BY15, BY20 and BY27). However, it was not possible to see any clear geographical pattern to this variation.

There was no seasonality in the deep water DSi concentrations. The only significant differences found in the mean concentrations are for stations BY15 (November; significantly higher than in March and April) and BY31 (January, significantly higher than April). In a long-term, the mean DSi concentrations were significantly higher before the salt water intrusion. The only exceptions are BY10 (t-test, $p = 0.175$) and BY30 (t-test, $p = 0.056$). For BY11 and BY21 the test was not performed as the time series start in 1992.

Changes in hydrography

DSi was positively, but not strongly, correlated with salinity ($r_P = 0.38$, $p < 0.001$) and temperature ($r_P = 0.24$, $p < 0.001$). There was a large increase in salinity after 1993 (Fig. 3). This clearly illustrates the effects of the large influx of saline, relatively oxygen rich, water in that year. Also changes in the O_2 and DSi concentrations were

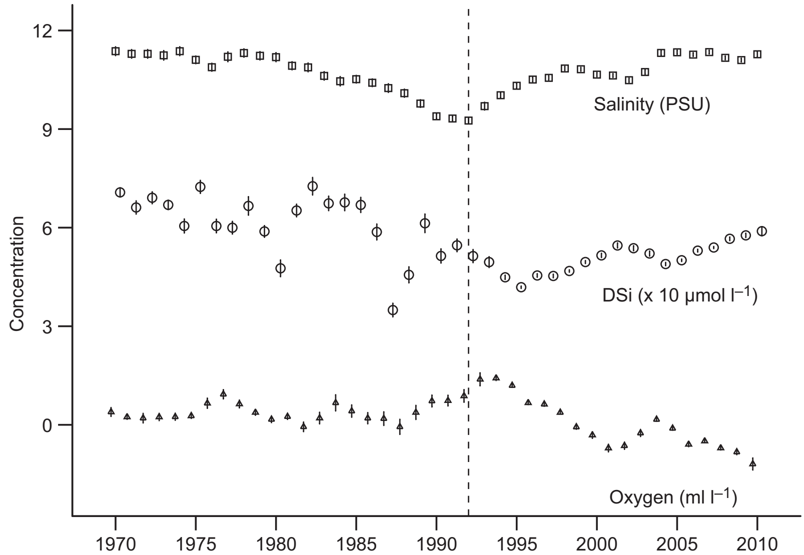

Fig. 3. 95% confidence intervals for DSi (circles), salinity (squares) and O_2 concentrations (triangles) over time. Note that DSi is multiplied by 10 to fit the scale.

apparent, although they seemed to lag behind the salinity increase. The year-to-year variation in the DSi concentrations was substaintial before 1992 as compared with that after 1992 (Fig. 3). Such patterns were not obvious in the other data, where the variations in salinity and O_2 concentrations over time were comparatively small. Two stations that contributed heavily to this effect were BY10 and BY30, at which large variations were recorded in the 1980s. No general geographical trend could be identified in the DSi levels measured at individual stations (Fig. 2).

Overall, the DSi concentrations were negatively, and strongly, correlated with O_2 (r_P = –0.65, $p < 0.001$). Stationwise, this relationship was even stronger and for a majority of the stations this relationship looked different in the two periods (Fig. 4).

Regression of depth-integrated mean concentrations

The regression model based on all the data examined in this study accounted for approximately half of the observed variation in DSi (r^2_{adj} = 0.50; Table 2). The DSi concentration decreased significantly with increasing O_2 concentration (β_1). It was also apparent that the 1992/1993 change had a significant impact on the relationship between the DSi and O_2 concentrations, in terms of both the intercept (β_2) and slope (β_3). On average, this decrease with O_2 was significantly greater before 1993 than after. If the conditions were to change from anoxic (i.e. an oxygen concentration of 0 ml l^{-1}) to oxic (oxygen concentration > 2 ml l^{-1}), the DSi concentration would be expected to decrease by 18 μmol l^{-1} under pre-1993 conditions as compared with 11 μmol l^{-1} for post-1993 conditions.

Stationwise, the strongest relationship between DSi and O_2 concentrations was found for BY11 (r^2_{adj} = 0.78; Table 2). For three other stations (BY15, BY19 and BY21) the regression model was able to explain more than 50% of the variation in DSi concentration. For the northernmost stations (BY27–BY30) and those in the southwest (BY34–BY36), however, the regression models did not account for a significant part of the DSi variation and some caution is necessary when interpreting the results from these stations. It should also be noted that for station BY34, there were no observations after 1992, while the data series for stations BY11, BY19 and BY21 started in 1992 (Table 1).

For the period 1993–2010, the intercept (β_0) and slope (β_1) parameters were similar for all the stations (Table 2). They were consistently lower than the corresponding parameters for the period between 1970 and 1992. For example, the intercepts for 1970–1992 were typically ca. 60, compared with ca. 50 for 1993–2010, while the slope

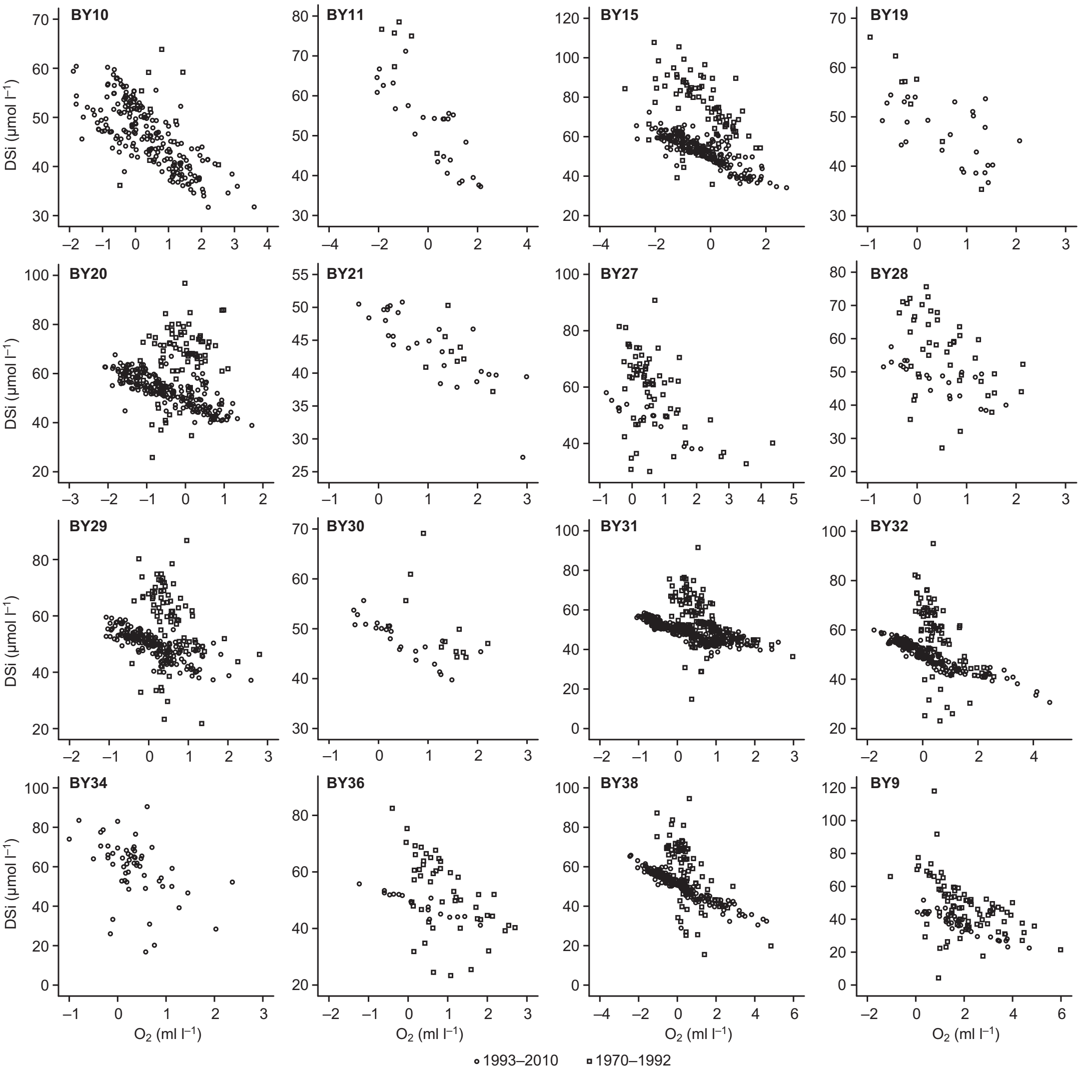

Fig. 4. DSi concentrations (µmol l^{-1}) *versus* O_2 concentrations (ml l^{-1}) at the studied stations. Filled squares are the data for the period 1970–1992 and circles for the period 1993–2010.

varied between –6.0 and –14.2 for 1970–1992, compared with –3.9 to –6.4 for 1993–2010. With the exception of station BY21, all stations were affected by the 1993 influx (Table 2). For some stations (BY9, BY10, BY27–BY30 and BY36), only the intercept changed significantly, with the slope remaining unchanged after 1993. At seven stations, the nature of the relationship between the DSi and O_2 concentrations changed significantly after the influx (Table 2). Notably, at stations BY11, BY19, BY31 and BY32, the decrease in DSi concentrations with increasing O_2 levels was almost twice as steep between 1970 and 1992 as compared with that in the period between 1993 and 2010.

Regressions at maximum depth

The regression analyses using only the measurements conducted at maximum sampling depth for each sampling event gave results similar to those obtained for the mean depth, but with a slightly higher coefficient of determination (r^2_{adj} = 0.62). The intercept was significantly higher for the period 1970–1992, while the regression coefficient for O_2 was significantly lower (Table 3). This was the same pattern as found for the mean data set, although more pronounced. This model indicated that when changing from anoxic to oxic conditions, DSi concentrations would decrease on average by 13 μmol l^{-1} during the period between 1993 and 2010, and by 20 μmol l^{-1} during the period between 1970 and 1992, or roughly by 0.8 μmol l^{-1} yr^{-1} as compared with 0.9 μmol l^{-1} yr^{-1}.

The strongest relationships were found for the stations in the deep Eastern Gotland basin, for which the r^2 values were greater than 0.8 (BY10–BY21; Table 3). These are the stations where bottom waters were found to be frequently anoxic (Table 1). The stations with comparatively low r^2 values, explaining one fifth of the observed variation in DSi, were mainly located in the northernmost region (BY27–BY29).

Once again, stations BY21 and BY34 were unaffected by the 1992/1993 break. For most stations, however, the intercept for the period between 1993 and 2010 was 20%–50% greater than that for 1970–1992. For approximately half of the stations studied, the decrease in DSi concentrations with increasing O_2 concentrations was significantly more pronounced in 1970–1992 than in 1993–2010. Remarkably, for stations BY20 and BY29, the slope parameter for the interaction variable is positive, indicating that changes in the O_2 concentration had a less pronounced effect on DSi concentrations during the period between 1970 and 1992 than between 1993 and 2010.

Discussion

The relationships between DSi and O_2 concentrations were very consistent among stations, as demonstrated by the similarities of the regression coefficients, even though the models indicate a stronger relationship in the eastern region.

There are a number of factors and processes that explain the variation in DSi and the strong relationship with O_2. They are, to some extent, controlled by the same physical factors (e.g. intrusion of saline waters) and biogeochemical processes (e.g. mineralisation of DSi) that will be discussed in the following sections.

Spatial variation in the observed silica concentrations

There is no obvious geographical pattern in the

Table 2. Regression results for the data set with mean values. DSi = $\beta_0 + \beta_1 O_2 + \beta_2 D_{70-92} + \beta_3 D_{70-92} \times O_2$, where D = 1 for 1970–1992 and 0 for 1993–2010. ns = not significant.

Station	$r^2_{adj.}$	β_0	β_1	β_2	β_3
All stations	0.503	50.3	–5.6	12.7	
BY10	0.541	48.3	–4.9	ns	6.1
BY11	0.775	53.1	–6.3	ns	–9.2
BY15	0.658	51.0	–6.2	20.3	ns
BY19	0.625	49.0	–3.9	4.7	–10.4
BY20	0.481	50.2	–6.2	15.6	11.3
BY21	0.600	49.1	–4.5	ns	ns
BY27	0.302	51.9	–7.1	11.5	ns
BY28	0.286	50.6	–6.9	8.8	ns
BY29	0.326	50.4	–6.0	10.6	ns
BY30	0.461	50.4	–5.7	7.4	ns
BY31	0.539	50.3	–5.7	12.5	–5.4
BY32	0.508	50.8	–4.5	13.0	–6.9
BY34	0.192	63.1	–11.6	ns	ns
BY36	0.270	50.8	–8.0	8.9	ns
BY38	0.572	51.2	–4.8	12.6	–5.7
BY9	0.348	48.3	–6.1	11.9	ns

Table 3. Regression analysis for the data set with observations at maximum water depth. DSi = $\beta_0 + \beta_1 O_2 + \beta_2 D_{70-92} + \beta_3 D_{70-92} \times O_2$, where D = 1 for 1970–1992 and 0 for 1993–2010. ns = not significant.

Station	$r^2_{adj.}$	β_0	β_1	β_2	β_3
All stations	0.617	51.4	–6.5	13.8	–3.1
BY10	0.824	52.6	–6.9	12.6	ns
BY11	0.894	54.4	–6.3	ns	–5.2
BY15	0.725	53.0	–6.6	25.9	–2.5
BY19	0.653	54.3	–8.2	ns	ns
BY20	0.586	51.6	–6.4	23.6	3.4
BY21	0.632	50.6	–4.9	ns	ns
BY27	0.240	51.1	–6.0	13.0	ns
BY28	0.198	50.1	–5.4	8.2	ns
BY29	0.387	50.8	–6.1	13.0	4.8
BY30	0.448	50.6	–6.4	8.0	ns
BY31	0.516	50.1	–5.5	11.8	–6.5
BY32	0.523	51.0	–4.5	12.7	–7.6
BY34	0.200	63.2	–12.0	ns	ns
BY36	0254	51.5	–8.6	9.5	ns
BY38	0.550	51.5	–4.8	12.9	–5.6
BY9	0.382	49.8	–6.6	13.4	ns

measured DSi concentrations. BY34 had a significantly higher mean concentration than the other stations, which might be because the only data for this station were acquired during the pre-1993 period when the DSi levels were comparatively high. The higher mean DSi concentrations for the first period are consistent with those reported in previous studies. DSi concentrations in the Baltic Proper were higher in the past than at present, and they are still decreasing (Papush and Danielsson 2006). Focusing on measurements acquired at water depths below 100 m, significant trends were previously found for stations BY15, BY27, BY31, BY32 and BY38. The DSi concentrations measured at these stations decreased between 1970 and 1990, and, for all stations but BY27, increased between 1993 and 2001 (ibid.). No such trends were found in the river DSi loads during these periods, indicating that the changes in DSi concentration in the bottom waters were probably unrelated to the external load.

There is a non-systematic difference in mean concentrations between stations that cannot be explained by location alone. A previous study by Rahm and Danielsson (2007) showed that in general, surface DSi concentrations on the western side of the Baltic Proper are considerably higher than those on the eastern side. However, they also found the DSi retention to be very low in the western side, indicating that DSi exported from the northern Gulf of Bothnia was generally transported southwards and out of the Baltic Sea through this region. The DSi residence times are longer in the central part of the basin than in the coastal areas (Papush *et al*. 2009) influencing the retention rate.

Changes in hydrography

Factors known to increase the rate of Si dissolution include salinity and temperature (Hurd 1983, Spencer 1983, Van Cappellen and Qiu 1997). Temperature changes did not seem to have a major effect on the data examined in this work (low correlation), while the correlation between salinity and DSi was somewhat higher. However, the consequences of salinity changes are demonstrated by the responses to the 1993 salt water intrusion. The present regression analyses showed that these intrusions had significant effects on the DSi concentrations at all stations; in general, the post-intrusion intercepts were lower and the decrease in DSi concentrations with increasing O_2 levels became less pronounced. In addition, the variation in the data decreased after the intrusion. When the deep water was replaced during major inflows, the water masses were forced upwards (Stigebrandt and Gustafsson 2007). These water masses contained large stocks of silica, and a result of these water masses being forced upwards could be a decrease in the DSi concentrations in the deep waters.

Another factor that may affect the DSi concentration is pH. At all stations and during all years examined in this work, pH varied between 7 and 8.3. DSi concentrations, however, did not correlate with pH ($r = -0.09$). This is consistent with the findings of Bauerfeind and von Bodungen (2006), who did not find any changes in BSi dissolution due to changes in pH (6.5–8.5).

Biogeochemical cycling

The regression analysis shows that the DSi concentrations significantly decreased with increasing O_2 concentrations. Previously Seiter *et al*. (2010) found a negative correlation between the benthic biogenic Si and O_2 fluxes. The higher Si concentrations in anoxic water are assumed to be due to biogeochemical processes that favour the export of DSi from the sediments (von Bodungen 1986, Berelson *et al*. 1987, Belias *et al*. 2007, Papush *et al*. 2009). In fact, Bauerfeind and von Bodungen (2006) suggested that anoxic conditions may enhance the dissolution of biogenic silica in the Baltic Sea compared to the North Atlantic.

There are several parallels between Si and P cycling. It has been suggested that the release of P from the sediments was more intense in the aftermath of the 1993 intrusion than at the end of the period of stagnation right before the intrusion (Conley *et al*. 2002). If dissolved P is not bound to stable compounds and buried, there may be a significant flux out of the sediments (Hille *et al*. 2005). Stigebrandt and Gustafsson (2007) found that shifts from oxic to anoxic bottoms within the Baltic Proper may potentially release up to 3g P m^{-2}. Rydin *et al*. (2011) calculated a long-term release rate of 1–2.7 g P m^{-2} yr^{-1}. No analogous estimates for Si have been reported.

As presented above, previous studies suggest that dissolution of biogenic silica is proportional to O_2 consumption, and the benthic Si fluxes are negatively correlated with the O_2 fluxes. Most of the stations examined in this work are located in hypoxic waters (Table 1), only three were located at sites where bottom water was mostly anoxic over the studied period (BY11, BY15 and BY20). The mean DSi concentrations measured at these three stations were significantly higher than those found at other stations (Fig. 2). The deep waters around station BY9, which is in the southernmost part of the Baltic Proper, are oxic almost 40% of the time, and have significantly lower mean DSi concentrations than most other stations. It is therefore reasonable to assume that the concentrations in the water mass largely reflect the variation in the O_2 conditions.

Diatoms dissolve, at least to some extent, in the water column or at the sediment–water interface. Bacterial activity can facilitate and control the process of silica dissolution on a micro-environmental scale by increasing the rate at which the organic layer covering the amorphous diatom shells is removed (Spencer 1983, Holstein and Hensen 2010). These effects might be significant in the Baltic Proper, which has significant bacterial production (Hagström *et al*. 2001). Sedimentation of spring diatoms, with subsequent mineralisation and dissolution of their Si, generates Si pulses in the sediment. Sufficiently large Si inputs could have a pronounced effect also on P dynamics, causing either an increased release of inorganic P or a change in the balance between dissolved organic P and microbial-bound particulate organic P (Kairesalo *et al*. 1995, in Tuominen *et al*. 1998). Numerous studies have shown that Si and P compete for sorption sites (e.g. Tuominen *et al*. 1998, Tallberg *et al*. 2008, Cornelis *et al*. 2011). Anions of both elements can adsorb to the surfaces of Fe- and Al-oxides. In fact, Brinkman (1993). found that 50%–60% of the extracted Si were found in fractions that are assumed to be Fe-bound.

Sediment fluxes may be an important internal source of DSi. Because of the ongoing decrease in Si concentrations, the mass of diatoms in the spring bloom is decreasing, which allows for an increase in the size of the cyanobacterial blooms in the summer (Heiskanen 1998, Wasmund and Uhlig 2003, Schneider *et al*. 2009). Drastic decreases in spring diatom blooms were first reported at the end of the 1980s (Wasmund and Uhlig 2003). These were assumed to be caused by mild winters preventing deep mixing, a necessity for diatom blooms. After the year 2000, the intensity of these diatom blooms increased (Wasmund *et al*. 2011), which is consistent with the negative trends in DSi concentrations presented in Papush and Danielsson (2006). In years with low production in spring, there was a corresponding high production in autumn. There also seems to be a negative relationship between diatom biomass and dinoflagellate biomass, with high dinoflagellate biomasses occurring in years with modest diatom blooms (Henriksen 2009, Wasmund *et al*. 2011). With the current low DSi levels, there are signs of Si limitation in some areas, which seem to be affecting both the quantity and quality of the diatoms in the spring blooms (Olli *et al*. 2008). This further highlights the importance of internal Si loads from sources such as anoxic areas (Papush *et al*. 2009), something also indicated in the present study.

Conclusions

The results reported herein provide quantitative information on the relationship between the concentrations of Si and O_2 within the bottom water of the Baltic Proper. The DSi concentrations were shown to decrease as the O_2 concentrations in the deep layers rise; this relationship was found for all the stations considered. The effects of a major salt water intrusion in 1993 were also investigated; it was found that the relationship between O_2 and DSi concentrations was strengthened by the influx. This relationship can be explained by the deep water exchange, as well as processes affecting mineralisation of DSi.

In an area where Si is rapidly becoming a seasonal limiting nutrient, sediments are an important internal source of silica. The hypoxic/anoxic conditions in the central and southern Baltic Proper could favour Si dissolution. The scope for combating eutrophication by oxygenating the bottom waters, and thereby increasing P retention, is being explored in a number of ongoing studies. The results reported here show that more studies on silica should be conducted before taking such action. It will be necessary to verify that oxygenation of the deep waters would not result in severe reductions in the biologically available Si, which would have adverse consequences on diatom production, or in increased P recycling due to competition for adsorption sites.

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